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(54) Supported catalyst for the (CO)polymerization of ethylene.

(57) A solid component of catalyst for the (co)polymerization of ethylene is composed of a silica support and of a catalytically active part containing titanium, magnesium, chlorine and alkoxy groups, and is obtained by:

(i) activating a silica support by contact with a solution of magnesium dialkyl, or magnesium alkyl chloride, in a liquid, aliphatic hydrocarbon solvent;

(ii) impregnating the activated silica with a solution, in a liquid aliphatic or aromatic ester, of titanium tetrachloride and tetra-alkoxide in equimolecular or almost equimolecular quantities, and magnesium chloride; and

(iii) treating the solid obtained in step (ii) with a proportioned quantity of aluminium alkyl sesquichloride.

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examples a microspheroidal silica is used as the support of the solid component in catalyst, in particles with an average diameter of 40 μm and having the following characteristics:

- apparent density:	0.21 g/ml
- surface area (BET):	320 m^2/g
- pore volume:	1.6 ml/g
- average pore diameter:	25 A

EXAMPLE 1

(i) 20 ml (17.5 mmoles) of 20% by weight $Mg(C_4H_9)_{1.5}(C_8H_{17})_{0.5}$ in n-heptane and 17 g of silica are charged, in a nitrogen atmosphere, into a 500 ml flask, equipped with a reflux cooler, mechanical stirrer and thermometer. The mixture is heated to 60 °C for 1 hour under stirring and the activated silica is then recovered by filtration.

(ii) 220 ml ethyl acetate, 4.96 g (14.6 mmoles) of titanium tetra n-butoxide, 1.6 ml (14.5 mmoles) of titanium tetrachloride and 2.79 g (29.4 mmoles) of magnesium chloride are charged, in a nitrogen atmosphere, into another 500 ml flask, equipped with a reflux cooler, mechanical stirrer and thermometer. The mixture is heated to reflux temperature (about 75 °C) for 1 hour until the magnesium chloride has completely dissolved. The activated silica is then added to the solution thus obtained as described in (i). Contact is left for 1 hour at 70 °C and the solution is then dried by evaporating the solvent.

(iii) The impregnated silica thus obtained is suspended in 300 ml of n-hexane and 8.81 g (35.6 mmoles) of aluminium ethyl sesquichloride are added to the suspension, at a temperature of 25 °C. The temperature is brought to 66 °C and the suspension is left to react for 1 hour.

(iv) At the end of this period the solid is recovered from the suspension, washed with anhydrous n-hexane until the chlorides have disappeared from the washing liquid, and finally dried.

28 g of a solid component of catalyst are obtained in the form of a microspheroidal solid, containing 4.3% by weight of titanium (19% of which is in the form of trivalent titanium), 3.8% by weight of magnesium, 18.4% by weight of chlorine and 2.2% by weight of aluminium.

EXAMPLE 2

Example 1 is repeated with the difference that in step (iii) 1.40 g of aluminium ethyl sesquichloride are used.

28.4 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.25% by weight of titanium (12% of which is in the form of trivalent titanium), 3.9% by weight of magnesium, 17% by weight of chlorine and 1.8% by weight of aluminium.

EXAMPLE 3

Example 1 is repeated with the difference that in step (iii) 13.2 g of aluminium ethyl sesquichloride are used.

28.0 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.3% by weight of titanium (38% of which is in the form of trivalent titanium), 3.4% by weight of magnesium, 19.3% by weight of chlorine and 3.5% by weight of aluminium.

EXAMPLE 4 (comparative)

Example 1 is repeated with the difference that in step (ii) 9.92 g (29.1 mmoles) of titanium tetra n-butoxide are used and titanium tetrachloride is not added.

28.5 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 3.7% by weight of titanium (43% of which is in the form of trivalent titanium), 3.8% by weight of magnesium, 12.4% by weight of chlorine and 1.7% by weight of aluminium.

EXAMPLE 5 (comparative)

Example 1 is repeated with the difference that in step (ii) 9.92 g (29.1 mmoles) of titanium tetra n-

butoxide are used and titanium tetrachloride is not added and in step (iii) 17.6 g (71.2 mmoles) of aluminium ethyl sesquichloride are used.

26.6 g of a component of catalyst are thus obtained in a microspheroidal form, containing 4.4% by weight of titanium (51% of which is in the form of trivalent titanium), 3.7% by weight of magnesium, 19.7% by weight of chlorine and 3.2% by weight of aluminium.

EXAMPLE 6 (comparative)

Example 1 is repeated with the difference that in step (ii) 5.50 g (29.0 mmoles) of titanium tetrachloride are used and titanium tetra n-butoxide is not added and in step (iii) 3.03 g (12.3 mmoles) of aluminium ethyl sesquichloride are used.

28.2 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.2% by weight of titanium (24% of which is in the form of trivalent titanium), 3.5% by weight of magnesium, 17% by weight of chlorine and 2.1% by weight of aluminium.

EXAMPLE 7 (comparative)

Example 1 is repeated with the difference that in step (ii) 5.50 g (29.0 mmoles) of titanium tetrachloride are used and titanium tetra n-butoxide is not added and in step (iii) the treatment with aluminium ethyl sesquichloride is omitted.

23.3 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.4% by weight of titanium (100% in tetravalent form), 3.8% by weight of magnesium and 13.7% by weight of chlorine.

EXAMPLE 8 (comparative)

Example 1 is repeated with the difference that in step (ii) 5.50 g (29.0 mmoles) of titanium tetrachloride are used and titanium tetra n-butoxide is not added and in step (iii) 6.03 g of aluminium ethyl sesquichloride are used.

24 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.1% by weight of titanium (35% of which is in the form of trivalent titanium), 3.6% by weight of magnesium, 19.4% by weight of chlorine and 2.4% by weight of aluminium.

EXAMPLE 9

The solid components of catalyst prepared in Examples 1-8 (tests 1-8) are used in polymerization tests of ethylene. More specifically, the polymerization is carried out in an autoclave having a volume of 5 litres containing 2 litres of n-hexane. The operating pressure is 15 bar in the presence of hydrogen, with a ratio between the hydrogen and ethylene pressure of 0.47/1, or 0.64/1, at a temperature of 90 °C and with a time of 1.5 hours, using aluminium triethyl as a co-catalyst, with a molar ratio between the aluminium triethyl and the titanium in the solid component of 50/1. Tests 9-11 are carried out with the solid component of catalyst of Example 1, but using a polymerization time of 3 hours.

Table 1 below shows, for each test, the ratio (RP) between the hydrogen pressure and the ethylene pressure; the yield (Yield) in polyethylene expressed in kg of polyethylene per g of solid component of catalyst; the yield with respect to the titanium (R/Ti) expressed in kg of polyethylene per gram of titanium in the solid component of catalyst; the density (D) of the polymer (ASTM D 1505) expressed in g/ml; the melt-flow index (MFI) of the polymer (ASTM D 1238; 2.16 kg and 21.6 kg) expressed in g/10 minutes; and the apparent density (AD) of the polymer (ASTM D 1895) expressed in g/ml.

Table 2 shows the particle size distribution expressed in μm, in % by weight of the polyethylenes obtained in the polymerization tests indicated in Table 1.

TABLE 1

Test	RP	Yield	R/Ti	D	MFI(2.16)	MFI(21.6)	AD
1	0.47	7.9	184	0.9627	6.5	208	0.36
2	0.47	1.85	44	0.9593	1.15	34.4	0.35
3	0.64	3.0	70	0.9665	7.0	160	0.32
4	0.47	4.2	113	0.9630	2.7	78.3	0.34
5	0.64	2.8	65	0.9641	4.8	137	0.36
6	0.64	2.2	53	0.9618	3.5	104	0.33
7	0.47	0.75	17	0.9545	0.82	25.9	0.34
8	0.64	2.0	48	0.9635	4.0	116	0.33
9	0.96	7.0	163	0.9673	32.8	ND	0.35
10	0.30	18.1	420	0.9638	4.1	129.7	0.39
11	0.21	27.4	794	0.9588	0.68	25.2	0.37

ND = not determined

TABLE 2

Test N.	Particle size (μm)					
	>2000	2000<>1000	1000<>500	500<>250	250<>125	<125
1	0.2	42.9	42.8	9.1	2.8	2.2
2	0.0	1.1	45.2	41.6	8.6	3.5
3	0.1	4.5	61.5	31.5	2.0	0.4
4	0.0	6.6	63.2	24.1	3.1	3.0
5	1.4	3.2	55.8	32.7	5.4	1.5
6	0.0	0.9	59.6	34.2	4.1	1.2
7	0.1	1.2	20.8	58.4	14.8	4.7
8	0.1	1.0	58.9	35.8	3.1	1.1
9	0.0	27.9	63.2	8.4	0.3	0.2
10	0.2	42.9	42.8	9.1	2.8	2.2
11	3.8	65.1	28.2	2.5	0.2	0.2

Claims

1. Solid component of catalyst for the (co)polymerization of ethylene, composed of a support of silica in small particles (50-90% by weight) and a catalytically active part (50-10% by weight) containing titanium, magnesium, chlorine, aluminium and alkoxy groups, obtained by:
   (i) activating a silica support by contact with a solution of magnesium dialkyl, or magnesium alkyl chloride, in a liquid aliphatic hydrocarbon solvent;
   (ii) impregnating the silica thus activated with a solution, in a liquid aliphatic or aromatic ester, of magnesium chloride and titanium tetrachloride and titanium tetra-alkoxide, operating with equimolecular, or almost equimolecular quantities of titanium tetrachloride and titanium tetra-alkoxide and with a molar ratio between the magnesium chloride and the titanium compounds of 1 to 10;
   (iii) treating the impregnated silica by contact with aluminium alkyl sesquichloride, operating with a molar ratio between the titanium compounds and the aluminium alkyl sesquichloride of 0.9:1 to 1.9:1; and
   (iv) recovering the solid component of catalyst from the reaction products of step (iii).

2. Solid component of catalyst according to Claim 1, wherein in step (i) the silica suitable as a catalyst support is preferably a microspheroidal silica (particle size 20-100 μm) having a surface area BET of 150 to 400 m^2/g, a total porosity of >80% and an average pore radius of 50 to 200 A.

3. Solid component of catalyst according to Claim 1, wherein in step (i) the magnesium dialkyl is selected from compounds which can be defined with the formula MgR'R", wherein R' and R", the same or different, each independently represent an alkyl group, linear or branched, containing from 1 to 10 carbon atoms and preferably from magnesium diethyl, magnesium ethyl butyl, magnesium dihexyl, magnesium butyl octyl, and magnesium dioctyl.

4. Solid component of catalyst according to Claim 1, wherein in step (i) the magnesium dialkyl or magnesium alkyl chloride is in a hydrocarbon solvent selected from pentane, isopentane, hexane, heptane and octane, at a temperature ranging from 40 to 100 °C, for times ranging from 0.5 to 2 hours and preferably at a temperature of 60 °C, for 1 hour.

5. Solid component of catalyst according to Claim 1, wherein in step (ii) the titanium tetra-alkoxide is selected from titanium tetra n-propoxide, titanium tetra n-butoxide, titanium tetra i-propoxide and titanium tetra i-butoxide.

6. Solid component of catalyst according to Claim 1, wherein in step (ii) an ester is used selected from methyl and ethyl esters of lower aliphatic carboxylic acids, chlorinated or not chlorinated, or from benzoic acid, preferably ethyl formate, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, ethyl chloroacetate, methyl benzoate and ethyl benzoate and more preferably ethyl acetate.

7. Solid component of catalyst according to Claim 1, wherein in step (ii) the operating temperature ranges from 50 to 100 °C, the times vary from 0.5 to 2 hours and preferably the temperature is about 70 °C, and the time about 1 hour.

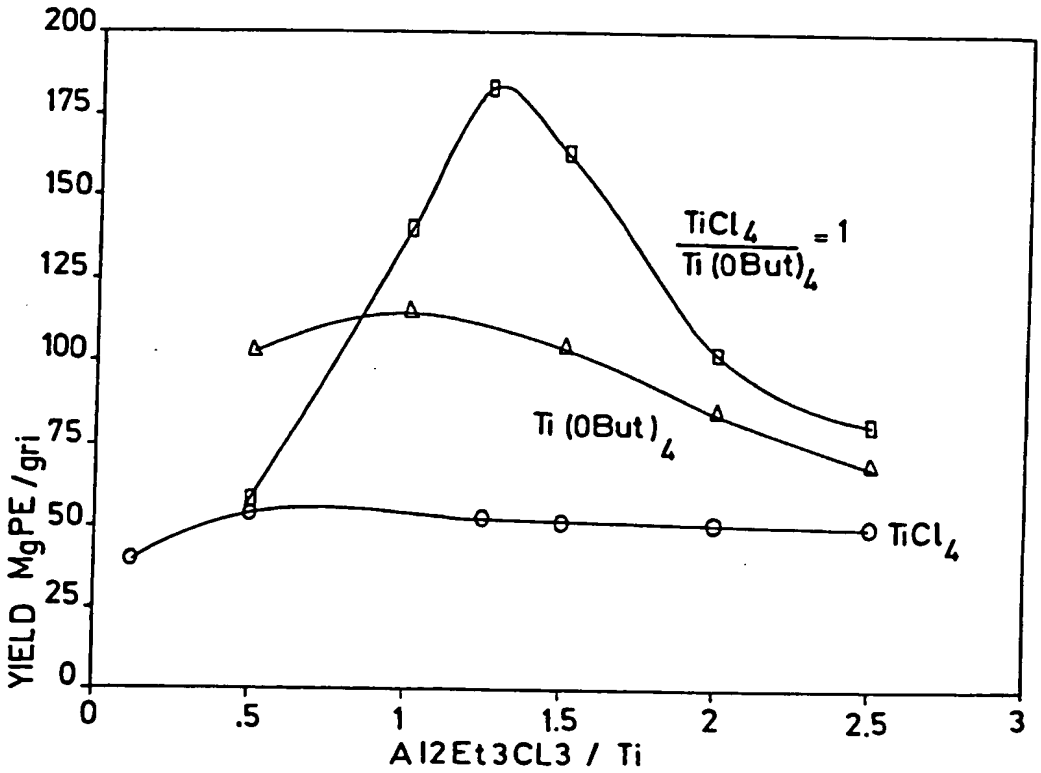
8. Solid component of catalyst according to Claim 1, wherein step (iii) is carried out with a solution of aluminium alkyl sesquichloride in a hydrocarbon solvent operating at a temperature ranging from 10 to 100 °C, for a time varying from 10 minutes to 24 hours, preferably from 20 to 90 °C, for a time of 15 minutes to 2 hours and in the more preferred method at 60-70 °C for about 1 hour, with a preferred molar ratio aluminium sesquichloride/titanium ranging from 1.1:1 to 1.7:1 and even more preferred from 1.2:1 to 1.3:1.

9. Solid component of catalyst according to Claim 1, containing 3-5% by weight of titanium, 3-5% by weight of magnesium, 15-20% by weight of chlorine, 1-5% by weight of aluminium, and 10-50% of the titanium being in its trivalent form, the remaining being in its tetravalent form.

10. Catalyst for the (co)polymerization of ethylene composed of the solid component of catalyst according to Claims 1 to 9 and of a co-catalyst aluminium trialkyl, alkyl aluminium hydride or aluminium alkyl halide.

11. Procedure for the (co)polymerization of ethylene using the polymerization catalyst according to Claim 10.

Fig.1


200
175
150
125
100
75
50
25
0
YIELD MgPE/gri
0
.5
1
1.5
2
2.5
3
Al2Et3CL3 / Ti
TiCl4 / Ti(OBut)4 = 1
Ti(OBut)4
TiCl4

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EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2060

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 463 672 (MONTEDIPE) * example 6 * * page 1 - page 3 *	1-3,5, 10-11 1-11	C08F4/656 C08F10/02
P,Y	EP-A-0 480 435 (ECP ENICHEM POLIMERI) * the whole document * & IT-A-21 711	1-11	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 DECEMBER 1992	FISCHER B.R.

CATEGORY OF CITED DOCUMENTS

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